

Bio-Inspired Carboxylate-Polymer/Metal Oxides Material for Electrocatalytic Water Oxidation

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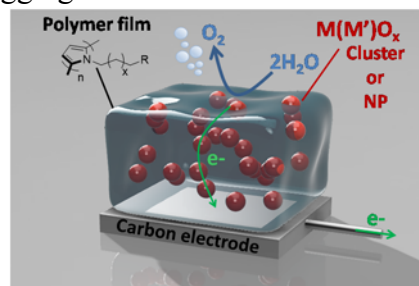
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Abstract

Water oxidation into dioxygen (OER) remains a bottleneck in the scale-up of water-splitting and CO₂-reduction electrolyzers due to slow kinetics and large overpotential. A key challenge is the development of efficient, robust and cheap OER catalysts, and heterogeneous metal oxides or (oxy)hydroxides are the most promising catalysts in terms of activity and robustness. Current research focuses on the development of oxides based on abundant metals (Co, Ni, Fe, Mn and Cu), which are less expensive than Ir and Ru oxides, and can be easily deposited on the surface of electrodes in the form of thin films to obtain efficient anodes.¹ A key factor in the performance of an electrocatalyst is its nanostructuration, the efficiency being significantly improved by increasing the active area/volume ratio while reducing the manufacturing cost. However, the reduction of the particles size to increase the specific surface area of the catalyst leads to a decrease of their stability and aggregation. These limitations can be overcome by immobilizing the nanoparticles (NPs) in a polymeric or inorganic material.²⁻⁴ In this context, we have recently designed bio-inspired nanocomposite electrode materials active and stable for water oxidation, by a simple and versatile electrochemical method. These new materials consist of (sub)nanosized earth-abundant (mixed) metal oxides M(M')O_x clusters (M, M' = Ni, Co, Fe...) well dispersed into a polymer matrix substituted with anionic functions,⁵ mimicking the carboxylates rich environment of the natural Mn₄CaO₅ cluster of PSII and its sub-nanosized structure, two essential features for an outstanding catalytic efficiency.



These composite materials have been characterized by several methods, such as SEM, TEM, AFM and GIWAXS. More recently, in-situ and ex-situ XAS studies have also been performed to further the analysis of the composite material. The method of elaboration of the nanocomposites, their characterization by several and complementary methods as well as their electrocatalytic performance for OER will be presented.

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Catalytic activity and mechanistic investigations of the nitrido Mo complex [(PPP)Mo(≡N)(I)] in the electrochemical reduction of N₂.

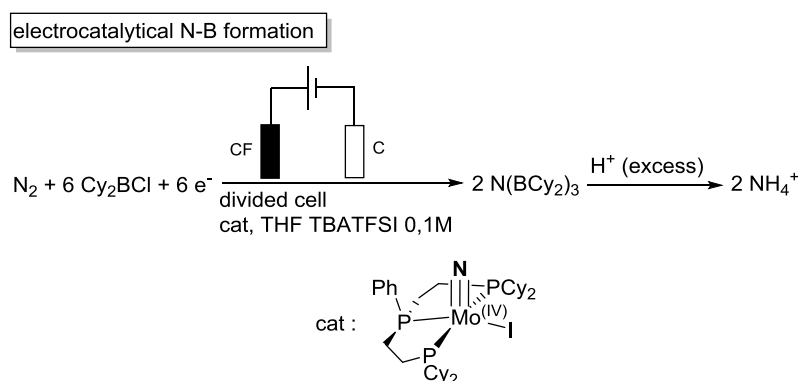
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The electrocatalytic reduction of N₂ (eN₂RR) by homogeneous metal complexes is currently considered as a promising alternative to the Haber-Bosch process, which is both energy intensive and most importantly a major CO₂ emission contributor. It opens up the possibility of replacing the harsh conditions used today in this industrial process with milder conditions involving renewable electricity sources.¹ Despite these advantages, very few molecular catalysts have so far proven effective for the electrochemical reduction of N₂, facing problems such as secondary reaction and low reactivity of N₂.^{2,3} To date, the most efficient example has been reported by Peters *et al.* with a faradaic yield of 44.5 %.⁴ In this presentation, we will present our recent work on the electrocatalytic reduction of N₂ using a (PPP)Mo(≡N)(I) catalyst developed by our group (see scheme below).⁵ We will show that chloroboranes can be used as a competent electrophile to react with the nitrogen atom bound to the Mo(IV) center. The properties of the catalyst and its role in the electrocatalytic transformation of N₂ into borylamine will be discussed on the ground of detailed electrochemical and spectroscopic data.⁶



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Comportement électrochimiques des quinones classiquement utilisées pour des applications bioénergétiques : considérations autour du côté anodique

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Dans le contexte environnemental et énergétique actuel, l'extraction de photocourants de l'activité photosynthétique a constitué un domaine de grand intérêt ces dernières années. C'est pourquoi de nombreuses approches ont été développées afin de mettre en œuvre une telle extraction d'électrons. Dans ce cadre, les dérivées de type quinone sont apparues comme étant des médiateurs particulièrement intéressants, notamment grâce à leur capacité à traverser les membranes. Dans de précédentes études, nous nous sommes intéressés au site cathodique de ce procédé, c'est-à-dire à l'étude de la capacité de ces dérivés à extraire ces électrons, et ce par des méthodes de fluorescence^(1,2) et électrochimiques⁽³⁾.

Le sujet de cette présentation sera l'étude de la capacité des dérivés de l'hydroquinone à être réoxydés à la surface de l'électrode, dans le but d'améliorer les performances du site anodique du procédé d'extraction des électrons photosynthétiques. Nous montrons ici que les propriétés thermodynamiques et cinétiques de ces molécules diffèrent grandement en fonction du dérivé choisi⁽⁴⁾. Nous montrons également que le prétraitement oxydatif de l'électrode, décrit par Ahammad & al⁽⁵⁾ comme un moyen d'accélérer la vitesse du transfert d'électrons du couple benzoquinone/hydroquinone, est efficace sur la majorité des dérivés mais pas sur les dichlorobenzoquinones, qui montrent un transfert d'électrons bien plus rapide⁽⁴⁾. Nous montrons également que suite à des limitations d'ordre cinétique, le nombre d'électrons échangé par molécule⁽⁶⁾ peut être intermédiaire entre 1 et 2⁽⁴⁾. Un modèle original est suggéré afin d'extraire des paramètres numériques permettant la comparaison entre les différentes quinones⁽⁴⁾.

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Controlled TEMPO-based layers for electrocatalysis application

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The electrocatalytic properties of the TEMPO group in the confined state has been previously exploited in our laboratory. To enhance the interfacial reactivity of the catalytic moiety, adjustments were made to surface properties, focusing on accessibility. The dilution of reactive species, investigated in the context of self-assembled monolayers (SAMs), has proven effective in boosting electrocatalytic activity⁽¹⁾. Facing the limitation of weak stability, diazonium chemistry, known for its robust attachment of organic moieties, has emerged as an alternative. Post-functionalization of reactive layers, formed through the reduction of diazonium salts, has been employed to elaborate TEMPO-diluted layers for electrocatalysis applications. However, in this case, the mixing of reactive centers with passive species did not lead to a reduction in steric constraints between catalytic species due to the disorganization of the material⁽²⁾. In our project, we introduce an innovative approach focused on the reduction of a diazonium mixture and allowing the precise control of surface properties while guaranteeing the stability of the mixed film. To implement this, we use an original molecular design for organic entities comprising an aryldiazonium cation, a spacer and the active group. Unlike the alkanethiols used in SAMs, the aryldiazonium cations serving as an anchoring group ensure strong fixation of the organic entities (Figure 1).

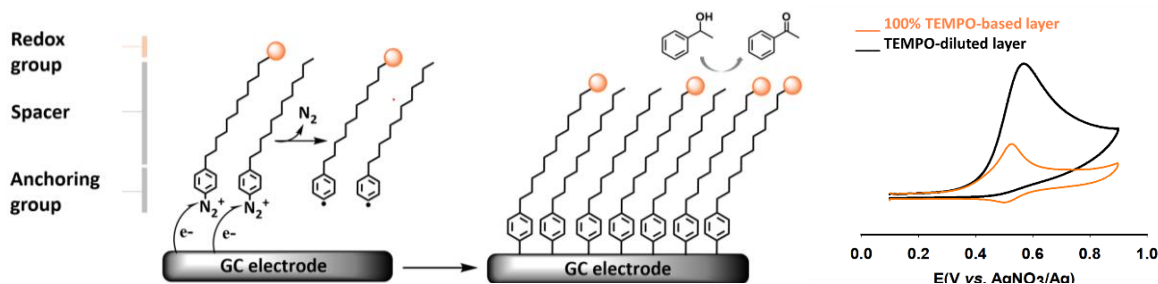


Fig. 1: TEMPO-diluted layer elaborated by co-reduction of diazonium mixture through proposed strategy, and its electrocatalytic response.

The insertion of an extended alkyl chain between the redox group and the aryl diazonium function allows striking at once the control over thickness, composition and organization of such mixed layers^{(3), (4)}, a challenge that is not overcome by conventional co-reduction of different diazonium salts designed without a spacer.

Two types of diazonium salts, one TEMPO-functionalized and the other used as a diluent, were designed based on the proposed template. Bi-component layers were elaborated through the simultaneous reduction of both diazonium salts. Then, we were able to explore the modulation of the dilution ratio of active species and evaluate the electrocatalytic performance on various TEMPO-diluted layers. Electrochemical and gravimetric studies conducted on the modified surfaces demonstrate the effectiveness of the proposed strategy to create sustainable TEMPO-based layers with significantly improved electrocatalytic activity.

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Effet de substituants et rôle d'un donneur de proton (H₂O) sur la réduction de N₂O par des complexes de rhénium

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Le protoxyde d'azote (N₂O) est un gaz à effet de serre 270 fois plus puissant que le dioxyde de carbone (CO₂), il représente 6% des émissions humaines totales. [1] Cela explique l'intérêt croissant donné à la réduction de N₂O.

Dans une étude préliminaire, nous avons montré que les complexes [Re(L)(CO)₃Cl] (L = 2,2'-bipyridine (bpy) et 4,4'-diméthyl-2,2'-bipyridine (dmbpy)) possèdent une activité catalytique à la fois efficace, stable et sélective pour la réduction de N₂O en N₂ en présence d'eau comme faible donneur de protons. [2] Le mécanisme de réaction a été étudié en détail, [2] montrant que l'étape clé est la génération de l'espèce bi-réduite [Re⁰(L^{•-})(CO)₃]⁻.

L'objet de la présente étude est (i) l'analyse de l'effet de la présence de différents substituants sur la bipyridine dans les complexes de rhénium (figure 1) vis-à-vis de l'activité des complexes pour la réduction de N₂O et (ii) l'analyse mécanistique du rôle du donneur de proton dans cette réaction de désoxygénation :

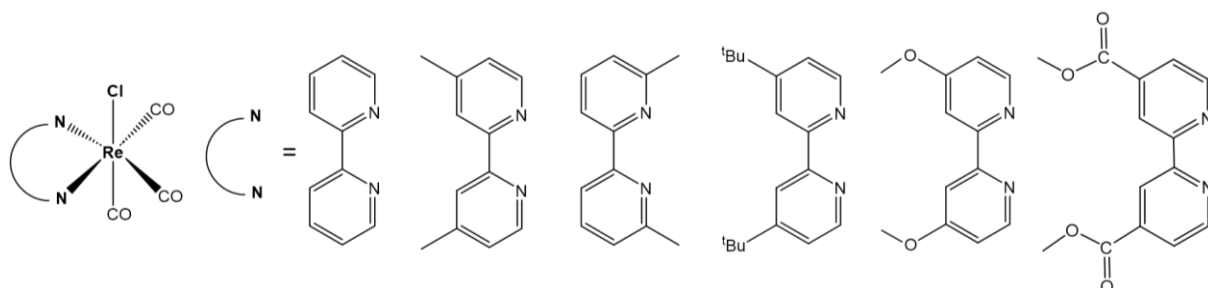
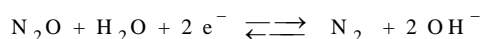


Figure 1. Complexes de rhénium étudiés

On montrera via une analyse cinétique par voltammétrie cyclique que les substituants donneurs (Me, ^tBu, MeO) ont un effet relativement modeste sur l'activité catalytique tandis que le substituant attracteur (CO(O)Me) inhibe la catalyse via une délocalisation des électrons sur le ligand.

On montrera également que la réaction de réduction de N₂O par l'espèce active électrogénérée [Re⁰(L^{•-})(CO)₃]⁻ est d'ordre 1 en donneur de proton (H₂O), celui-ci est donc crucial dans le processus de rupture de la liaison N-O. L'eau joue également un rôle dans la génération électrochimique de l'espèce active [Re⁰(L^{•-})(CO)₃]⁻, modulant ainsi la surtension nécessaire à la catalyse.

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Elaboration et Caractérisation d'Électrocatalyseurs à base de {Mo₃S₄} pour la Réaction d'Evolution d'Hydrogène (HER)

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Le recours aux sources d'énergies propres, sûres et efficaces est une nécessité [1,2]. Dans ce contexte, l'hydrogène constitue une solution prometteuse à condition que ce dernier soit produit à partir de procédés non émetteurs de CO₂. L'électrolyse de l'eau, plus précisément l'électrolyse de l'eau à membrane échangeuse de protons (PEM) est une méthode efficace pour la production d'hydrogène de grande pureté et adaptée au couplage avec des sources intermittentes d'énergie renouvelable. Cependant, cette technologie requiert l'emploi de catalyseurs de type platinoïdes (PGM) pour les deux demi-réactions de production d'oxygène OER (*i.e.* IrO₂) et de production d'hydrogène HER (*i.e.* Platine) [1,3].

Dans cette communication, nous présenterons nos récentes avancées ayant pour but de remplacer les catalyseurs à base de Pt par des catalyseurs à base de métaux non critiques (*e.g.* Mo, W). Nous nous intéresserons plus particulièrement à l'élaboration de catalyseurs à base de {Mo₃S₄} emprisonnés dans une matrice tungstique. Ces nouveaux matériaux W_x - Mo₃S₄ peuvent être vus comme des solides étendus analogues aux systèmes moléculaires {Mo₃S₄}-polyoxométallates connus pour leurs excellentes propriétés électrocatalytiques [4,5]. A titre d'exemple, nos catalyseurs W_x - Mo₃S₄ montrent une surtension cathodique de 137 mV avec une pente de Tafel de 37 mV.dec⁻¹.

Pour étudier plus avant cette nouvelle classe de catalyseurs HER, nous nous intéressons à leurs caractérisations *in-situ* notamment en couplant la microscopie à force atomique (AFM) à la microscopie électrochimique à balayage (SECM) (*c.f.* figure). Cette technique AFM-SECM permet de corrélérer les propriétés topographiques, nano-mécaniques et électrochimiques à l'échelle du site actif. De plus, l'emploi de pointes AFM-SECM ayant une taille de 25 nm permet d'atteindre une très bonne résolution d'images par rapport à l'utilisation d'un SECM classique [6].

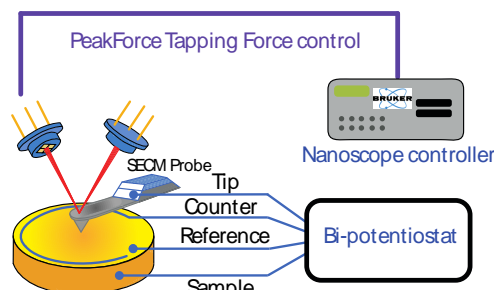


Figure montrant le principe de fonctionnement de l'AFM-SECM [6].

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Electrocatalytic hydrogenation of biomass-derived furfural on structured copper electrodes

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The rapid electrification and defossilization of chemical processes is a cornerstone of all net zero emission scenarios, with the aim of rapidly and drastically curb CO₂ emissions tied to climate change. To accomplish this objective, electrically-powered alternatives to petrochemical processes for the production of carbon-based compounds must be developed. One attractive approach is to directly employ “green electrons” produced from renewable energy sources to power the electrocatalytically-driven chemical transformations of molecules

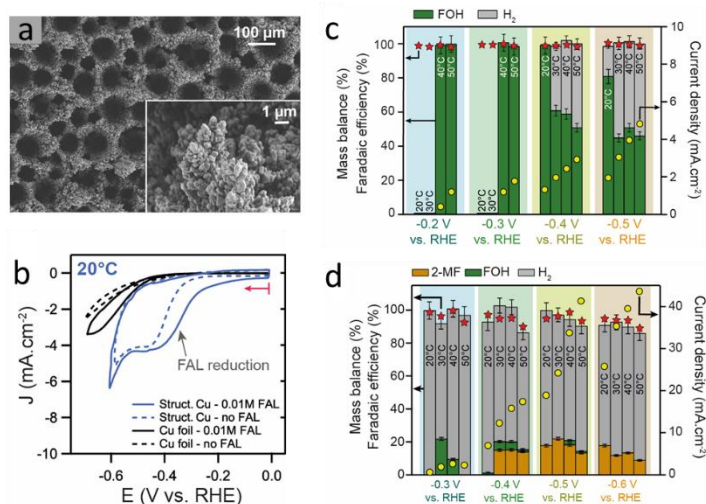


Figure 1 a) SEM pictures of structured Cu electrodes b) Cyclic voltammograms obtained for Cu foil and structured Cu electrodes in the absence and presence of furfural (FAL) in 0.1M potassium phosphate (pH 7.0). Electrocatalytic performance (faradaic efficiency = bars, mass balance = red stars, current density = yellow markers) obtained at pH 7.0 (c) and pH 1.0 (d) in the presence of furfural, as a function of potential and temperature (FOH: furfuryl alcohol, 2-MF: 2-methylfuran).

obtained from lignocellulosic biomass.¹ Here, we describe our recent progress using structured copper electrodes for the efficient and selective electrocatalytic hydrogenation of furfural towards furfuryl alcohol or 2-methylfuran.² Structured Cu electrodes (see **Figure 1a**) were developed and applied to the ECH of furfural (an attractive biomass-derived chemical already produced on a large scale). These structured electrodes were tested in neutral and acidic conditions, and displayed tunable selectivity and activity with the pH and temperature. **Figures 1b-d** summarize the electrocatalytic performance we measured under different conditions of pH, potential and temperature, showing

significant improvement over a Cu foil reference, representative of the current state of the art.³ In particular in neutral condition where furfural was selectively converted to furfuryl alcohol at potentials as high as -0.2 V vs the reversible hydrogen electrode (RHE), while 2-methylfuran could also selectively be obtained under acidic conditions, albeit with a stronger competition from H₂ evolution. We further employed an innovative quasi in-situ photoelectron spectroscopy approach to characterize the nature of adsorbed carbon-containing compounds at the surface of the electrode under operating conditions, allowing to point towards difference in mechanisms between furfural reduction in neutral and acidic conditions.

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Electrodes métalliques imprimées en 3D par fusion laser pour l'électrolyse alcaline de l'eau

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La production d'hydrogène connaît un fort regain d'intérêt depuis la mise en place de stratégies nationales et internationales visant à la décarbonation des activités pour des besoins industriels (production d'ammoniac) et mobiles (véhicules)¹. Les solutions les plus développées sont basées sur des électrolyseurs en milieu acide, qui nécessitent l'emploi de métaux nobles comme le Pt ou le Ru. Si les milieux alcalins permettent d'atteindre des densités de courant moins importantes, ils ouvrent la possibilité d'utiliser des métaux de transition, parmi lesquels le Ni est une bonne base d'électrode². Il est souhaitable de moduler les densités d'états d'énergie de ses orbitales d pour imiter les métaux nobles et catalyser les réactions de production d'H₂ (HER) et d'O₂ (OER)^{3,4}. En parallèle, le récent procédé d'impression 3D métallique SLM (Fusion Laser Selective) permet d'obtenir des électrodes avec des géométries complètement nouvelles et des alliages de compositions maîtrisées^{5,6}. Nos travaux exploitent la méthodologie des plans d'expériences⁷ pour isoler les meilleurs alliages binaires microstructurés imprimés en 3D sous forme cylindrique du Ni avec du Co, Fe, Mo, Cr à une échelle semi-appliquée (25 cm² ; 50 mA cm⁻²) pour l'électrolyse alcaline (KOH 1 M) de l'eau (**Fig. 1**).

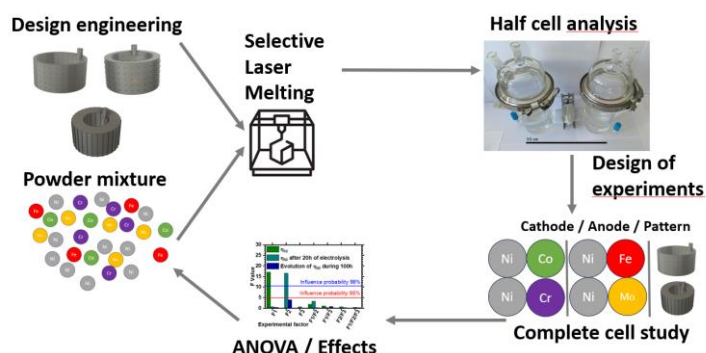


Figure 1 – Principe d'étude des électrodes binaires microstructurées imprimées en 3D

Avec des rendements Faradiques de plus de 90% vs Pt et vs IrO₂/RuO₂, nous avons réussi à obtenir des surtensions abaissées de 460 mV à 50 mA cm⁻². Les meilleurs systèmes se sont dégradés de moins de 30 mV en une semaine et le meilleur assemblage cathode : anode : motif d'électrode (NiCo : NiMo : trous coniques) a consommé moins de 50 kWh/kg d'H₂ produit, se rapprochant des objectifs de l'Union Européenne pour 2030 (48 kWh/kg).

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Enhancing homogeneous electrochemiluminescence with freely diffusing $[\text{Ir}(\text{sppy})_3]^{3-}$ complex - theoretic insights

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Electrochemiluminescence (ECL) is the light emission arising from the radiative decay of the luminophore's excited state that is populated through a redox reaction of electrochemically produced radicals.¹ It has emerged as a sensitive analytical technique with various applications.² Yet, enhancing its efficiency relies on a fundamental understanding of its underlying mechanisms. Here, we explored the mechanisms behind low potential ECL amplification in the model ECL coreactant system, consisting of tris(2,2'-bipyridine)-ruthenium ($[\text{Ru}(\text{bpy})_3]^{2+}$) luminophore and tripropylamine (TPrA) sacrificial coreactant, upon the addition of a water-soluble redox-active Ir(III) complex - tris(2-(2-pyridinyl- κ N)-4-sulfonate phenyl- κ C)iridium(III) ($[\text{Ir}(\text{sppy})_3]^{3-}$).³⁻⁵ The cascade of redox reactions following the electrochemical oxidation of the Ir mediator, coreactant, and luminophore produce $[\text{Ru}(\text{bpy})_3]^{2+*}$ and $[\text{Ir}(\text{sppy})_3]^{3-*}$ excited electronic states, which emit light (at $\lambda_{\text{max}} = 620$ nm and 515 nm, respectively) upon relaxation.

Through electrochemical methods, spectroscopy and finite element simulation, we demonstrated that low-potential ECL emission is governed by three kinetically limited reactions, which modulate the concentration ratio of radical species. Namely, oxidation reactions facilitated by Ir(III) lead to the production of TPrA radicals and excited $[\text{Ru}(\text{bpy})_3]^{2+*}$ states, enhancing ECL intensity. Conversely, $[\text{Ir}(\text{sppy})_3]^{2-}$ reacting with TPrA radicals resulted in ECL quenching. Finally, we investigated the interplay between the key reaction steps, showing that the mediator's redox properties dictate ECL behaviour: ECL onset and peak potential, maximal intensity and spatial extension of the light-emitting layer. Thus, the developed model aids in both understanding and predicting ECL dynamics in the presence of redox mediators with distinct redox properties, manifesting the potential for tailored ECL systems with improved performance in analytical, imaging and biomedical applications.

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Films-fins électroniquement actifs pour de nouveaux concepts de nanodispositifs

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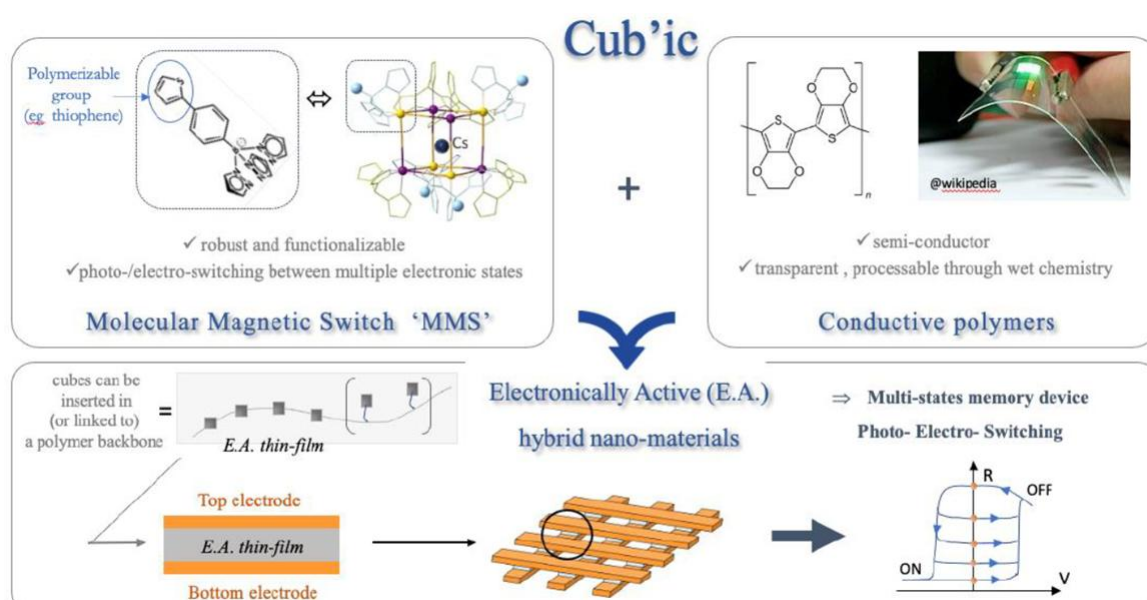
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Résumé

La déposition sur surface de molécules fonctionnelles, en mono- ou multicouches, est investiguée de façon intensive avec pour objectif de les intégrer dans des dispositifs électroniques miniaturisés, sans tenter de concurrencer les technologies à base de Silicium. Le projet mis en place dans l'ANR Cub'ic, propose d'utiliser des cubes moléculaires électroactifs présentant plusieurs états redox stables (complexes polymétalliques Fe, Co) pouvant être utile en électronique moléculaire, en optoélectronique mais aussi en spintronique grâce à des complexes à transitions de spins. Ces cubes possèdent également l'avantages de posséder des groupements électropolymérisables tels que les thiophènes ou encore les EDOTs leur permettant d'être déposé sur surface conductrice afin de construire, *in fine*, les dispositifs autour de ces couches moléculaires. L'électropolymérisation et l'électrocaractérisation de ces objets seront ici présentées, montrant l'influence des ligands polymérisables présents sur les arêtes de ces cages moléculaires. Puis, les propriétés physico-chimiques des couches déposées seront étudiées avant la construction de nanodispositifs adaptés.



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Glucose Electroreforming on Nickel-based nanoparticles optimized *via* design of experiments

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In a context of climate change, hydrogen is considered as one of the main candidates for the energy transition. To date, about 4% of its production comes from renewable energy sources¹. Water electrolysis has been developed for decades but the kinetics for the oxygen evolution reaction is known to be sluggish, and requires high anode potentials to occur (i.e. high cell voltage and energy cost). Among other alternatives, it is possible to produce clean hydrogen through biomass valorization (e.g. from agricultural or paper industry waste). In this process, hemicellulose and lignin are decomposed into platform molecules such as monosaccharides, e.g. glucose and xylose, which can in turn be converted into hydrogen and value-added compounds by electrolysis.

Glucose and xylose electrooxidation can be carried out using non-noble metals such as nickel, which could make it possible to move away from the use of PGMs in clean hydrogen production. However, synthesis of non-noble metal nanoparticles tends to result in larger particle sizes compared to PGM materials. Therefore, the optimization of the synthesis of transition metal nanoparticles is needed. The polyol method is known to give highly crystalline, monodispersed and small size nanoparticles, even with transition metals, and is convenient for upscaling².

In this work, a systematic approach thanks to the concept of design of experiments was adopted for the synthesis of metallic nickel nanoparticles supported on carbon by polyol method. Optimal synthesis parameters were determined to respectively minimize nickel mean crystallite size, increase the electrochemical surface area (ECSA), and enhance the current density for glucose electrooxidation at selected potential of 1.5 V vs. RHE, i.e at least 200 to 300 hundred mV lower than that for OER in alkaline media.

Experimental conditions of this work enabled the formation of face centered cubic metallic nickel nanoparticles without addition of external reducing agents, surfactants or seeding agents. Obtained particles possess a high electrochemical surface area and are active for glucose electrooxidation. The use of a experiments design successfully highlighted a set of conditions leading to the best compromise between mass activity and potential for scalability.

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Electrochemical and structural study of NiRu_x heterofunctional catalysts for the alkaline HER

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The alkaline water electrolysis is a promising method to store intermittent energy sources while producing green hydrogen efficiently. Among the different technologies available, anion exchange membrane (AEM) electrolyzers has the advantage of functioning with catalysts based on non-noble metals. Indeed, the use of alkaline medium provides suitable chemical stability for a large range of materials such as transition metals, which significantly reduces the AEM cost and allows a large-scale use. However, the performances and stability observed for AEM catalytic films are lower due to the sluggish water dissociation step occurring during the hydrogen evolution reaction (HER). Therefore, the concept of heterofunctional catalysts emerged as an efficient approach to combine the properties of active materials and create a synergy between them in order to promote the dissociation of water. To do so, members of our team developed a new family of heterofunctional catalysts based on large particles of nickel decorated by ruthenium nanoparticles. XPS results indicate that ruthenium is mostly observed on the nickel surface, which supports a heterogeneous structure. We carried out electrochemical characterizations (cyclic voltammetry measurements and electrolyzer test) and the results showed very high efficiencies for this family of materials (see figure 1.a), with performances similar to the platinum ones (60% Pt/C). The materials structure was also analyzed by operando X-Ray Absorption Spectroscopy (XAS) at the Ni and Ru K-edges to identify which metals are involved in the catalysis at low and high ruthenium content (see figure 1.b). In this presentation, the electrochemical and XAS results will be presented as well as the relationship between the structure and activity of these materials.

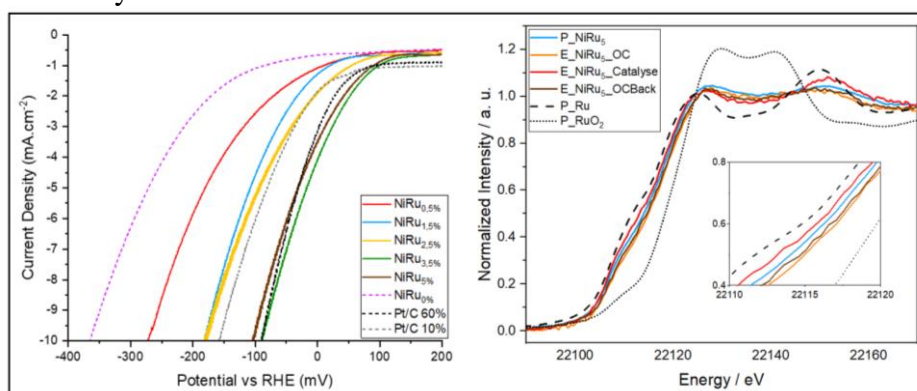


Figure 1:(a) cyclic voltammograms of the NiRu_x and Pt/C 10% and 60% wt. references in 0.1 M KOH; (b) Operando XANES spectra registered for the NiRu_{5%} and the references.

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Impact of weak halogen bond interactions on the activity of iron porphyrin catalysts for the electrochemical CO₂-to-CO conversion

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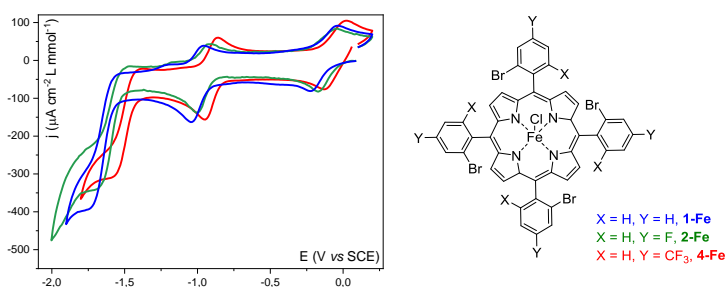
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Environmental challenges related to the increasing levels of CO₂ are nowadays a big issue for humanity. Among the possible approaches, the electrochemical reduction of CO₂ is a promising and greener way to obtain industrial products, thus contributing to the development of a circular economy.

In this context, iron porphyrins can play an important role as catalysts for the selective reduction of CO₂-to-CO.¹ In the past years, many studies have pointed out the role of peripheral substituents on the core ligand in favouring the interaction between CO₂ and the iron at the centre of the macrocycle for boosting the redox-mediated electrochemical CO₂ reduction. Notably, the important role of moieties that can establish cooperative hydrogen bond or coulombic interactions has been demonstrated.^{2,3}

In this work we are investigating the role of halogen bonding (XB) as a through-space interaction able to promote the catalytic reduction of CO₂ in the presence of iron porphyrin catalysts. XB can be defined as a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophile.⁴ In the present study several halogenated iron porphyrins have been synthesized, characterized and tested as catalyst for CO₂ reduction. We will present evidence for the enhanced catalytic activity of iron porphyrins due to secondary sphere coordination effects via intramolecular XB.



Scheme 1. CV of brominated iron porphyrins under CO₂

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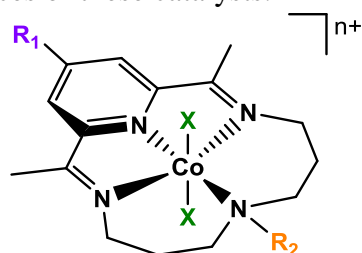
Modulating HER and CO₂RR performances of cobalt tetraaza-macrocyclic complexes through ligand substitution

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As the demand for more efficient and environmentally friendly energy solutions grows to address current environmental challenges, the development of efficient catalysts for Hydrogen Evolution Reaction (HER) and/or CO₂ Reduction Reaction (CO₂RR) has become essential. Among the various systems proposed for this purpose, cobalt catalysts featuring tetraaza-macrocyclic ligands, particularly those with pyridyl-diimine patterns (CoCR14) first isolated in the 1969,¹ show considerable promises. Despite being only recently applied in both electro- and photo-catalytic HER² and CO₂RR³ in homogeneous solutions, these catalysts exhibit remarkable efficiencies, with CoCR14 recognized as one of the most effective and stable catalysts in aqueous solutions for HER.⁴ To enhance catalytic efficiency and tailor the selectivity of this system, our team aims to expand this family of catalysts by incorporating different functional groups at the ligand's periphery, as it has only been done rarely but showed remarkable effect.⁵ This presentation will focus on the preparation of several CoCR14 complexes, introducing various electron-withdrawing/donating moieties at the *para* position of the pyridine to modulate the complex's redox properties. Additionally, we will look into the introduction of branching groups at the secondary amine position, potentially serving as proton relays to facilitate H₂ formation. The effects of these modifications will be investigated through spectro-electrochemistry, providing insights into the electro-/photo-catalytic performances of these catalysts.



X = Cl, MeCN

R₁ = Electron-withdrawing/donating groups

R₂ = Proton relay

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New Mixed-Sandwich Dawson Type Polyoxotungstates [(Ni-H₂O)₂Cu₂(As₂W₁₅O₅₂)₂]¹⁶⁻ and [(Cu-H₂O)₂Ni₂(As₂W₁₅O₅₂)₂]¹⁶⁻: redox behaviors and electrocatalytic properties

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One of the solutions to the use of fossil fuels explored is the exploitation of electrochemical reactions around dihydrogen (Hydrogen Evolution Reaction, HER) and dioxygen (Oxygen Evolution Reaction or Oxygen Reduction Reaction, OER and ORR)⁽¹⁾. These are often slow reactions that need to be activated. Thus, it is necessary to synthesize suitable electrocatalysts. Today, the most efficient electrocatalysts are those based on noble metals, but these have many shortcomings: their price, their scarcity and the difficulty in recycling them.

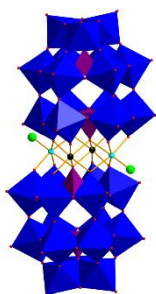
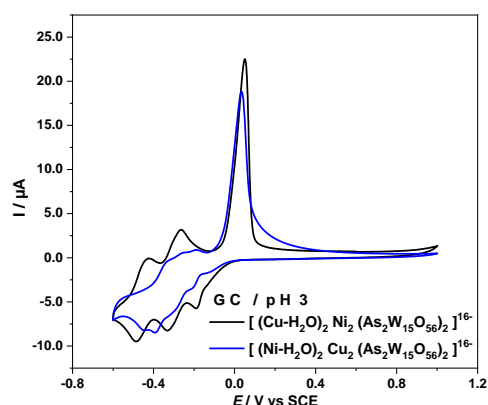


Figure 1: Polyhedral representation of the mixed STP

Polyoxometalates (POMs) are anionic inorganic complexes capable of fast and reversible multiple electron transfers. The great variations in their compositions imply multiple possibilities for their properties. In particular, they have already shown interesting performances for electrocatalysis^(2,3) worth exploring. To do so, a new method of synthesis for Mixed Sandwich Type Polyoxometalates (STP), in which selected metallic centers of interest are associated, has been developed. In contrast with the procedures⁽⁴⁾ that have been described so far, this one is a one-step or one-pot procedure, saving time, energy and reagent and exhibiting good yields. Among the library of compounds whose synthesis was either improved or described for the first time, we present here two new STPs : [(Ni-H₂O)₂Cu₂(As₂W₁₅O₅₂)₂]¹⁶⁻ and [(Cu-H₂O)₂Ni₂(As₂W₁₅O₅₂)₂]¹⁶⁻.

The metallic core, made of Nickel and Copper ions in different positions, is “sandwiched” between two tungstic POM fragments, [As₂W₁₅O₅₆]¹²⁻. In addition to their electrochemical characterization in different media, their electrocatalytic properties towards ORR and HER are assessed by Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV). Interesting effects due to the different combinations are shown.

Figure 2 : Cyclic voltammograms of the two STPs in pH 3 media (0.2M Li₂SO₄ + H₂SO₄) ; [STP]: 2.10⁻⁴M ; scan rate: 20 mV/s; working electrode : glassy carbon ; reference electrode : SCE



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Oxygen Reduction Reaction electrocatalysis enhanced by functionalized plasmonic Gold Nanorods

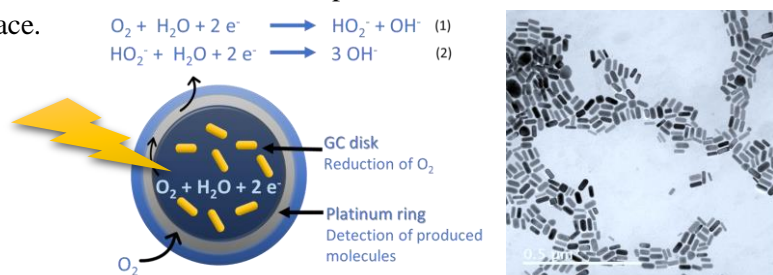
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Nowadays, developing “green” fuel cells is of paramount importance, where the activation of O₂ via electrochemical reduction is revealed to be a promising alternative to energy conversion technologies. Oxygen reduction reaction (ORR) plays a crucial role in fuel cells and requires an efficient electrocatalyst that could undergo multielectron exchange processes. Au-based and Ag-based spherical nanoparticles functionalized through reductive grafting with calix[4]arene diazonium salts have been already demonstrated to exhibit high catalytic performance and good durability compared to their citrate analogs.¹

This work explores the electrocatalytic properties of gold anisotropic nanomaterials, which were synthesized via the seed-mediated growth method. Absorption properties of gold nanorods (AuNRs) stabilized by CTAB, citrate, and calix[4]arene-tetradiazonium salt were measured via UV-visible absorption spectroscopy while their morphology and structure were examined via high-resolution transmission electron microscopy (HRTEM). The hybrid interface was thoroughly characterized by combining Raman spectroscopy and theoretical calculations. We will show that by using organic macrocycles able to form a strong covalent bond with the metallic surface, we can control the structure of the interface of the AuNRs at the molecular scale, and this could be effective for electrocatalysis.

Besides, one further interest in anisotropic nanomaterials is the variability of their plasmonic properties. They exhibit strong visible-spectrum absorption due to their localized surface plasmon resonances (LSPR) excitation. The UV-visible spectra revealed two absorption peaks due to the anisotropic nature of nanorods: a small peak at 519 nm, dedicated to the excitation of a localized surface plasmon resonance (LSPR) transverse band, which is a short axis and less dense, and an intense absorption peak at 642 nm of the longitudinal band on the long axis. Electrocatalytic reactions could benefit from plasmonic effects to boost performance.² The electrocatalytic properties toward ORR of AuNRs capped with CTAB or modified with Calix[4]arene-tetradiazonium macrocycles were studied with and without laser irradiation at different wavelengths. Selectivity and efficiency of the hybrid materials were compared. The stability of the two series of AuNRs upon irradiation will be discussed, considering the nature of the interface.



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Radical Scavengers: Keys to Deciphering and Controlling Oxygen Reduction at Platinum Electrocatalysts

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The oxygen reduction reaction (ORR) plays a pivotal role in electrochemical systems, significantly influencing energy conversion technologies such as electrolysis, fuel cells, and metal-air batteries. Historically, (Pt) electrocatalysts have been favored due to their relatively high activity but their lack of stability remains an important issue that is still not well understood.¹ Focusing on the ORR mechanism, it involves complex multiple pathways,² encompassing intricate surface interactions and various soluble reactive intermediates including radical species that could be responsible of the Pt degradation.

In this study, we propose to investigate the role of radical scavengers such as TEMPO or DMPO with the objectives of: i) controlling the production of reactive intermediates, and ii) gaining a comprehensive understanding of the steps driving ORR efficiency. As shown in the Figure, Our approach involves a combination of techniques: the scanning electrochemical microscope (SECM) in a generation-collection mode to probe electroactive intermediates generated during the ORR,³ electron paramagnetic resonance (EPR) spectroscopy to identify the reactive oxygen species resulting from their adducts formed with the radical scavengers,⁴ and numerical simulations to quantitatively describe the reaction. Through this approach, we aim to offer a quantitative understanding of the ORR mechanism and to control the reactivity of the reactive oxygen species.

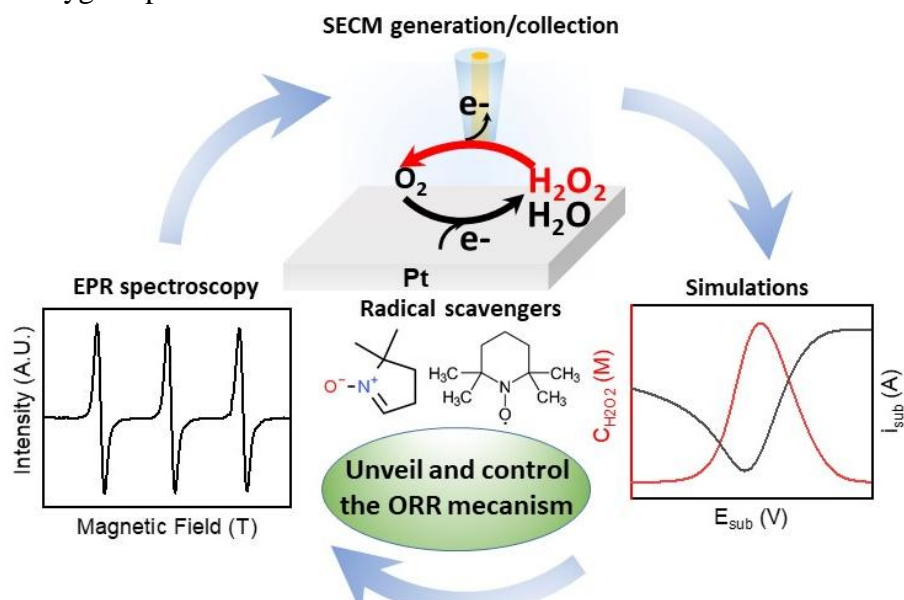


Figure: Strategy explored to decipher and control the ORR at Pt electrocatalyst

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Rhodium- and cobalt-based cathodes with low metal loading for electrocatalytic hydrogen evolution under neutral pH conditions

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With the increasing availability of electricity produced from renewable energy sources (e.g. sun and wind), water electrolysis has emerged as a viable technology for the clean production of hydrogen (H₂).¹ Electrocatalysis of the H₂ evolution reaction (HER) at both noble metal and noble metal-free cathodes has been extensively investigated under strongly acidic or alkaline pH conditions, where it is the most efficient. However, the setting-up of H₂ production systems working at very low or very high pH entails several practical drawbacks, especially those linked to corrosion.

On the other hand, HER electrocatalysts able to work under kinetically unfavorable neutral/near-neutral pH conditions have been scarcely investigated.² Importantly, such electrocatalysts might be suitable for integration into hybrid biological inorganic (HBI) systems, which have the potential to overcome the challenges facing “pure” biological or inorganic systems for carbon dioxide (CO₂) and nitrogen (N₂) fixation.³

In this context, we report here preliminary results on the HER at neutral pH by rhodium and cobalt-based cathodes with low metal loading. The electrodes were prepared by reacting a solution of pentamethylcyclopentadienide 1,10-phenanthroline-5,6-diamine complex of Rh or Co with an oxidized carbon surface leading to the attachment of the metal complex through covalent and conjugated bonds.⁴ This approach, related to that of Surface Organometallic Catalysis (SOMCat),⁵ offers the prospect of synthesizing electrocatalysts in which the chemical environment of dispersed single metal sites is well-controlled and remains well-defined. A rhodium-based cathode prepared by this method with metal loading as low as 6.6 10⁻³ mg cm⁻² has already shown its efficiency and stability for the HER under strongly acidic pH conditions.⁶

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Step-by-step electrochemical nitrogen reduction through Mo-N-H_x intermediates

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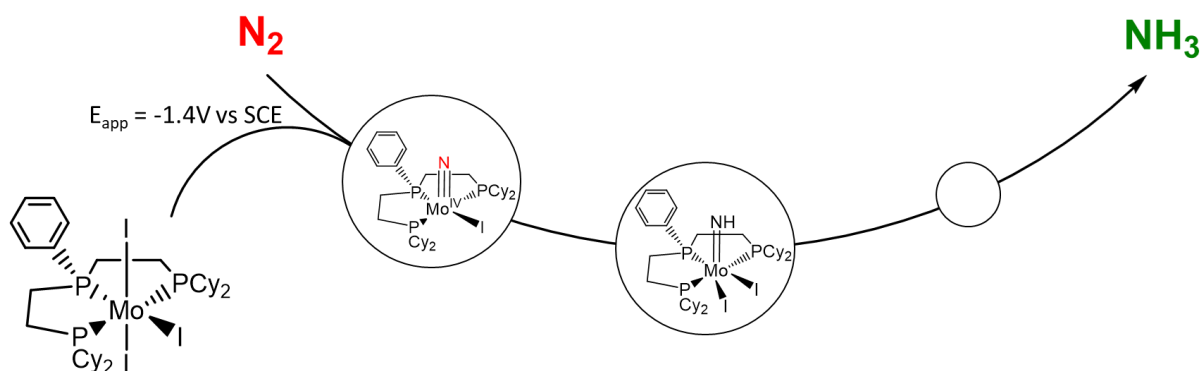
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One of the current challenges in chemistry is the (photo-)electrochemical production of ammonia (NH₃) from atmospheric dinitrogen (N₂) in conditions of ambient temperature and pressure, without using molecular H₂ or emitting CO₂ due to the intensive energy process, as an alternative to the Haber-Bosch process. Indeed, this later process accounts for about 1% of the worldwide energy consumption per year and nearly 1.5% of the worldwide production of CO₂ per year.

The nitrogen reduction reaction ($N_2 + 6H^+ + 6e^- \rightarrow 2NH_3$) implies a series of elementary steps that require a delicate balance of reactivity at the metal active site M (cleavage of the N-N triple bond without creating a too strong, poisoning M-N interaction; avoiding competitive reduction of protons to H₂ ...)^{(1),(2)}. To date, examples of molecular electrocatalysts including abundant metals remain scarce, although recent spectacular progress has been made, notably with Fe and Mo based catalysts^{(3),(4)}. In this communication, we will present and discuss the electrochemical reduction of nitrogen through different Mo-N-H_x intermediates along step-by-step PCET, using a Mo Pincer complex analog to those having been shown to produce ammonia in homogeneous catalysis⁽⁵⁾.



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